PATENT SPECIFICATION

NO DRAWINGS

Inventors: JOSEPH PARK and MALCOLM GORDON STEWART

1157320

1157320

Date of filing Complete Specification: 4 March, 1968.

Application Date: 14 March, 1967. *No. 11956/67.*

Complete Specification Published: 9 July, 1969.

Index at acceptance: —C3 F(1A1A, 1A3, 1B1, 2D2, 2F, 2G, 3D, 3E, 3F, 3H, 3L); C2 C(P3B11A, P3B15A, P3B16, P3B18B, P3B18D, P3B21, P1LZ, 1Q4, 1Q6A1, 1Q6A2, 1Q6B1, 1Q6B2, 1Q6C, 1Q7B, 1Q8A, 1Q9B, 1Q9D1, 1Q9D2, 1Q9D3, 1Q9F1, 1Q9F2, 1Q11D, 1Q11F, 1Q11G, 1Q11H, 1Q11J, LQ20Y, LQ30Y, LQ32Y, LQ321, LQ36Y, LQ360, LQ361, LQ366, LQ368, LQ491, LQ620, LQ623, LQ638); C3 P(4C6B, 4C14B, 4C16A, 4C16B, 4C20C, 4C20D1, 4C20D2, 4C20D3, 4D3B1, 4K10, 8C6B, 8C8B, 8C8C, 8C16A, 8C16B, 8C20C, 8C20D1, 8C20D2, 8C20D3, 8D2B2, 10C6B, 10C14B, 10C16A, 10C16B, 10C20C, 10C20D1, 10C20D2, 10C20D3, 10D1A, 10K4): C3 R(20P, 27K8D)

Int. Cl.: —C 08 b 21/09; 27/44; C 08 f 29/00; 45/36

COMPLETE SPECIFICATION

Improved Film-Forming Compositions

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to film-forming compositions modified by the inclusion of fluorine-containing ester to enhance their stain resistance and oil, grease and water repellency.

Film-forming polymeric materials such as, for example, cellulose esters and ethers, polymethyl methacrylate, polyvinyl acetate or polyvinyl chloride are commonly used in lacquer compositions for surface coatings. We have now discovered that films having enhanced resistance to staining and improved oil and grease repellency may be obtained by mixing certain fluorine-containing esters with the film-forming polymeric material in the lacquer or film-forming composition.

Thus in accordance with the invention a film-forming composition comprises a film-forming polymeric material and a fluorine-containing ester containing a chain of at least three carbon atoms in which at least half of the carbon valencies other than carbon to carbon are satisfied by a fluorine atom, the quantity of ester being such that the fluorine content of the composition is in the range 0.1 to 30%, and preferably 1—2%, by weight of the total solids.

The fluorine-containing chain may be provided by either the acid or the alcohol from which the ester is derived or both portions may contain a fluorine-containing chain. A convenient ester, in which the fluorine containing chain is provided by the acid portion of the ester, may be derived from a fluorine containing carboxylic acid of the formula R^F—COOH wherein R^F denotes a fluorinated alkyl group. Preferably the R^F group is a straight or branched chain alkyl group of 4 to 18 carbon atoms in which at least half, and preferably all, of the hydrogen atoms are replaced by fluorine atoms. Convenient R^F groups include perfluorobutyl and perfluoroheptyl and a bis-(2-pentafluoroethyl)-2-trifluoromethyl ethyl group. The fluorine-containing esters may conveniently be esters of the acids R^F—COOH with a mono- or polyhydric alcohol. Preferred alcohols include castor oil, ethylene glycol, polyethylene glycol, glycerol, trimethylolpropane, trimethylolethane, mono- and dipentaerythritol, trimethylol amino methane and diethylene glycol monoether.

A convenient ester, in which the fluorine-containing chain is provided by the alcoholic portion of the ester, may be derived from a primary, secondary or tertiary alcohol. Alcohols of the formula $R^F(CH_2)_nOH$, wherein R^F denotes a fluorinated alkyl group and n is an integer from 1 to 3, give especially useful compositions. Preferably the R^F group in the above formula is a straight or branched chain alkyl group of 3 to 18 carbon atoms

ERRATA SLIP ATTACHED

wherein at least half, and preferably substantially all, of the hydrogen atoms are replaced by fluorine atoms. Conveniently the R^F group may be perfluoropropyl, perfluorobutyl, perfluorohexyl, perfluorooctyl or perfluorodecyl group. The fluorine-containing esters are conveniently esters of these alcohols with any of the aforementioned fluorine-containing carboxylic acids or with any other inorganic or carboxylic acids (or the anhydrides or halides of such acid). Suitable acids include, for example, phosphoric, phthalic, adipic, sebacic, tartaric, citric, stearic and abietic acid and the adduct of abietic acid and maleic anhydride. The esters formed from polybasic acids may, if desired, be partial esters although completely esterified compounds are preferred.

The preferred film-forming polymeric materials include nitrocellulose, cellulose acetate, cellulose acetate butyrate, ethyl cellulose, polymethyl methacrylate, polyvinyl chloride and polyvinyl acetate, and copolymers thereof.

In addition to the polymeric film-forming material and the fluorine-containing ester, the film-forming compositions may contain other modifying ingredients such as are commonly used in film-forming compositions. These include plasticisers, slip agents, anti-settling agents, pigments, resins and waxes. The film-forming compositions may be prepared as lacquer solutions by dissolving in solvents, and applied to surfaces such as of wood, paper, leather or metal, by brushing, spraying or other spreading means to give, on drying, a film having enhanced stain and soil resistance and oil, grease and water repellency.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight.

EXAMPLE 1

The nitrocellulose used in this Example had a nitrogen content 11.6 and 12.2% and was 'damped' with isopropanol in the ratio 70 parts nitrocellulose to 30 parts isopropanol. 40 g. of this nitrocellulose dried and dissolved in 100 cc. aqueous acetone, prepared by mixing 95 volumes acetone and 5 volumes water, had a viscosity of 8 to 13 poises at 20°C.

Resin A was a non-drying coconut oil modified glyceryl phthalate resin containing 31% fatty acid, 46% phthalic anhydride and having an acid value of 14.5 to 23.5 mg. KOH/g.

Resin B was a butylated urea/formaldehyde resin ("Beetle" (Registered Trade Mark) BE 640) used as a 60% solution in butanol.

Preparation of fluorine-containing ester

68 parts of pentaerythritol, 207 parts of pentadecafluorooctanoic acid and 20 parts of xylene were mixed in a stirred reaction vessel fitted with a Dean and Stark apparatus and a gas inlet. Carbon dioxide gas was passed in at a rate of 10 cc. per minute and the temperature raised to reflux and maintained thereat for 1 hour.

The vessel contents were cooled to 100°C, 84 parts of acetic anhydride added, and a porous thimble containing anhydrous sodium sulphate placed in the reflux line. Heating was resumed and reflux maintained for a further 5 hours.

Xylene and excess acetic anhydride were removed under vacuum to give 285 parts of pentaerythritol triacetate monopentadecafluorooctanoate (43% fluorine) as a white waxy solid.

Lacquer preparation

The ester prepared above was incorporated into a lacquer having the following composition:—

	Parts
Nitrocellulose	24 (as dry)
Resin A	36
Resin B	30
Di-isooctyl phthalate	9
Pentaerythritol triacetate monopentadecafluorooctanoate (43% F) (as prepared above)	1
Dibutyl and monobutyl acid phosphates (Equimolar mixture)	3
Solvent	200

The solvent composition was:—

	Parts
Butyl acetate	30
Ethyl acetate	18
n-butanol	12
66 O.P. Industrial Methylated Spirits	4
Xylene	15
Toluene	15
Ethylene glycol monoethyl ether	6

The lacquer was sprayed on to a wood substrate to give a film. This film showed improved soil, water and grease resistance when compared with films made from the same formulations omitting the fluorine-containing ester.

EXAMPLE 2

Preparation of fluorine-containing ester

14.8 parts of phthalic anhydride, 117.0 parts of alcohol of formula $H(CF_2)_{10}CH_2OH$ and 40 parts xylene were mixed in a stirred vessel fitted with a reflux condenser and gas inlet. Carbon dioxide was passed in at a rate of 10 cc. per minute and the temperature raised to reflux and maintained thereat for 12 hours.

The product was isolated by removing the xylene under vacuum to give 102 parts of fluoroalkyl phthalate as an off-white waxy solid containing 60% fluorine.

Lacquer preparation

The ester prepared above was incorporated into a lacquer having the following composition:—

	Parts
Nitrocellulose (as used in Example 1)	24
Resin A (as used in Example 1)	36
Resin B (as used in Example 1)	30
Di-isooctyl phthalate	8
Fluoroalkyl phthalate containing 60% F (as prepared above)	2
Dibutyl and monobutyl acid phosphate (Equimolar mixture)	3
Solvent	200

The solvent composition was:—

	Parts
Butyl acetate	30
Ethyl acetate	18
n-butanol	12
66 O.P. Industrial Methylated Spirits	4
Xylene	15
Toluene	15
Ethylene glycol monoethyl ether	6

The lacquer was sprayed on to wood and gave a film of improved soil, water and grease resistance as compared with a film made from the same formulation but omitting the fluorine-containing ester.

EXAMPLE 3

Preparation of fluorine-containing ester

29.6 parts of phthalic anhydride, 146 parts of alcohol of formula $H(CF_2)_6CH_2OH$ and 0.1 g. of p-toluene sulphonic acid were mixed in a stirred reaction vessel fitted with a reflux condenser and a gas inlet. Carbon dioxide was passed in at a rate of 10 cc. per minute and the temperature raised to reflux and maintained thereat for 13 hours.

166 parts of fluoroalkyl phthalate were obtained as a straw-coloured liquid having a fluorine content of 46.6%.

Lacquer preparation

The liquid ester prepared above was incorporated into a lacquer having the following composition:—

	Parts
Nitrocellulose (as used in Example 1)	40 (as dry)
Resin A (as used in Example 1)	40
Di-isooctyl phthalate	14
Fluoroalkyl phthalate containing 46.6% F (as prepared above)	6
Solvent	150

The solvent composition was:—

	Parts
Butyl acetate	9
Ethyl acetate	25
n-butanol	5
Toluene	50
Isopropanol	11

The lacquer was sprayed on to a heavy cardboard and showed superior soil, water and grease resistance when compared with a film made from the same formulation but omitting the fluorine-containing esters.

EXAMPLE 4

Preparation of fluorine-containing ester

13.45 parts of triethylene glycol, 34.22 parts of perfluorooctanoyl chloride and 10.0 parts of pyridine were heated with 50 parts of toluene in a stirred reaction vessel fitted with a reflux condenser. The temperature was raised to reflux and maintained thereat for 10 hours. The contents of the vessel were cooled and extracted with water until free from pyridine hydrochloride. Toluene was removed under vacuum to give 35.5 parts of triethylene glycol monopentadecafluorooctanoate as a pale yellow liquid of fluorine content 49.6%.

Lacquer preparation

The product prepared above was incorporated into a lacquer having the following composition:—

	Parts
Nitrocellulose as used in Example I except that the viscosity of the solution of 40 g. (dry) in aqueous acetone was between 30 and 50 poises at 20°C	24 (as dry)
Resin A (as used in Example 1)	36
Resin B (as used in Example 1)	30
Di-isooctyl phthalate	8
Triethylene glycol monopentadecafluorooctanoate (49.6% fluorine) (as prepared above)	2
Dibutyl and monobutyl acid phosphates (Equimolar mixture)	3
Solvent	300

The solvent composition was:—

	Parts
Butyl acetate	30
Ethyl acetate	18
n-butanol	12
66 O.P. Industrial Methylated Spirits	4
Xylene	15
Toluene	15
Ethylene glycol monoethyl ether	6

The lacquer was sprayed on to wood to give a film with improved soil, water and grease resistance as compared with a film made from the same composition from which the fluorine-containing ester was omitted.

EXAMPLE 5

Preparation of fluorine-containing ester

20 parts of a polyethylene glycol having a molecular weight of about 800 and 21.60 parts of pentadecafluorooctanoic acid were refluxed with 500 parts of dry toluene in a stirred reaction vessel fitted with a porous thimble containing anhydrous sodium sulphate in the reflux line. Reflux was maintained for 12 hours. The toluene was removed by distillation and the product dried in vacuo to give 30 parts of polyethylene glycol pentadecafluorooctanoate as a pale yellow liquid with a fluorine content of 12%.

Lacquer preparation

The product prepared above was incorporated into a lacquer having the following composition:—

	Parts
Nitrocellulose as used in Example 1 except that the viscosity of the solution of 40 g. (dry) in aqueous acetone was 3 to 5 poises at 20°C	40 (as dry)
Resin A (as used in Example 1)	40
Polyethylene glycol pentadecafluorooctanoate (Fluorine content 12%) (as prepared above)	24
Solvent	120

The solvent composition was:—

	Parts
Butyl acetate	9
Ethyl acetate	25
n-butanol	5
Toluene	50
Isopropanol	11

The lacquer was sprayed on to cardboard and gave a film with improved soil, water and grease resistance as compared with a film made from the same composition except that the fluorine-containing compound was omitted.

EXAMPLE 6

Fluorine-containing alkyl phthalate containing 60% fluorine as prepared in Example 2 from the alcohol $H(CF_2)_{10}CH_2OH$ was made into a lacquer having the following formulation:—

	Parts
Nitrocellulose (as used in Example 1)	40 (as dry)
Resin A (as used in Example 1)	40
Di-isooctyl phthalate	18
Fluoroalkyl phthalate containing 60% F	2
Solvent	150

The solvent composition was:—

	Parts
Butyl acetate	9
Ethyl acetate	25
n-butanol	5
Toluene	50
Isopropanol	11

The lacquer was sprayed on to wood to give a film which had improved soil, water and grease resistance as compared with a film made from the same composition from which the fluorine-containing ester was omitted.

EXAMPLE 7

Preparation of fluorine-containing ester

A fluoro-alcohol acid phosphate was prepared in the following manner:—

35 parts of an alcohol having the formula $H(CF_2)_8CH_2OH$ were mixed with 5 parts phosphorus pentoxide and were heated under reflux for 20 minutes, then filtered, giving a filtrate having an acid value of 140 mg. KOH/g. and containing a phosphate ester. The ester was orthophosphoric acid in which one or two hydrogen atoms were substituted by a fluoro-alcohol group, giving a partial ester.

Lacquer preparation

The phosphate prepared above was incorporated into a lacquer composition having the following composition:—

	Parts
Nitrocellulose (as used in Example 1)	24 (as dry)
Resin A (as used in Example 1)	36
Resin B (as used in Example 1)	30
Di-isooctyl phthalate	10
Fluoro-alcohol mixed acid phosphate (60% F)	10
Solvent	230

The solvent had the following composition:—

	Parts
Butyl acetate	30
Ethyl acetate	18
n-butanol	12
66 O.P. Industrial Methylated Spirits	4
Xylene	15
Toluene	15
Ethylene glycol monoethyl ether	6

The lacquer was brushed on to wood and gave a film with improved soil, water and grease resistance as compared with a film made from the same lacquer composition from which the fluorine-containing ester was omitted.

EXAMPLE 8

A lacquer having the following composition was prepared:—

	Parts
Cellulose acetate powder having an acetyl value of 35%	70
Trichloroethyl phosphate	30
Fluorine-containing alkyl phthalate containing 60% fluorine (as prepared in Example 2)	1.7
Solvent	400

The solvent composition was:—

	Parts
Acetone	50
Ethyl acetate	15
Toluene	15
66 O.P. Industrial Methylated Spirits	15
Ethyl lactate	5

The lacquer was applied to cardboard by brushing and gave a film with improved soil, water and oil resistance as compared with a film made from the same composition from which the fluorine-containing ester was omitted.

EXAMPLE 9

A lacquer having the following composition was prepared:—

	Parts
Cellulose acetate powder having an acetyl value of 35%	70
Trichloroethyl phosphate	30
Pentaerythritol triacetate monopentadecafluorooctanoate (as prepared in Example 1)	2.2
Solvent	400

The solvent composition was:—

	Parts
Acetone	50
Ethyl acetate	15
Toluene	15
66 O.P. Industrial Methylated Spirits	15
Ethyl lactate	5

The lacquer was applied to cardboard by brushing and gave a film with improved soil, water and grease resistance in comparison with a film from the same composition but from which the fluorine-containing ester was omitted.

EXAMPLE 10

Resin C used in this Example was a castor oil alkyd containing 45% fatty acid, 41% phthalic anhydride and having an acid value 40—47 mg. KOH/g. A 50% solution in xylene had a viscosity of 36—60 poises at 20°C.

A lacquer of the following composition was prepared:—

	Parts
Cellulose acetate butyrate containing approximately 37% butyryl, 13% acetyl and 2% hydroxyl	15
Resin C	10
Pentaerythritol triacetate monopentadecafluorooctanoate (fluorine content 43%) (as prepared in Example 1)	0.5
Toluene	37
Butanol	7
66 O.P. Industrial Methylated Spirits	7
Butyl acetate	16
Ethylene glycol monobutyl ether	5
Ethylene glycol monobutyl ether acetate	3

The resultant lacquer was sprayed on to a polished aluminium surface and gave a film which was superior in soil, water and grease resistance to a film made from the same composition from which the fluorine-containing ester was omitted.

EXAMPLE 11

The ethyl cellulose used in this Example contained 47.5 to 49.0% ethoxyl. A solution of 5 g. in 100 cc. of a mixture of 80 volumes toluene and 20 volumes ethanol and a viscosity of 8 to 11 centipoises at 25°C.

The Resin D used in this Example was Cellolyn 102, a modified pentaerythritol ester of rosin, having an acid value of 35 mg. KOH/g. (Cellolyn is a registered Trade Mark).

A lacquer having the following composition was prepared:—

	Parts
Ethyl cellulose	18
Dicyclohexyl phthalate	3.4
Resin D	4.5
Pentaerythritol triacetate monopentadecafluorooctanoate (as prepared in Example 1)	3
Toluene	42
66 O.P. Industrial Methylated Spirits	10.6
Xylene	14
Butanol	3.5

The resultant lacquer was sprayed on to cardboard and gave a film of improved soil, water and grease resistance as compared with a film made from the same composition but from which the fluorine-containing compound is omitted

EXAMPLE 12

A lacquer of the following composition was prepared:—

	Parts
Ethyl cellulose (as used in Example 11)	18
Dicyclohexyl phthalate	3.4
Resin D (as used in Example 11)	4.5
Fluorine-containing alkyl phthalate containing 60% fluorine (as prepared in Example 2)	2
Toluene	42
66 O.P. Industrial Methylated Spirits	10.6
Xylene	14
Butanol	3.5

The resultant lacquer was sprayed on to cardboard and gave a film of improved soil, water and grease resistance as compared with a film made from the same composition but from which the fluorine-containing compound is omitted.

EXAMPLE 13

A lacquer of the following composition was prepared:—

	Parts
Vinylite VYHH (Vinylite is a Registered Trade Mark) (A polyvinyl chloride/ polyvinyl acetate copolymer containing 83% vinyl chloride and having an intrinsic viscosity in cyclohexanone at 20°C of 0.53)	20
Pentaerythritol triacetate monopentadecafluorooctanoate (as prepared in Example 1)	2
Toluene	40
Methyl ethyl ketone	20
Methyl isobutyl ketone	20

The resultant lacquer was sprayed on to wood and gave a film with improved soil, water and grease resistance as compared with a film made from the same composition from which the fluorine containing ester was omitted.

EXAMPLE 14

Preparation of fluorine-containing ester

37.36 parts of castor oil, 16.56 parts of pentadecafluorooctanoic acid and 10 parts of xylene were added to a stirred reaction vessel fitted with a gas inlet and a porous thimble containing anhydrous sodium sulphate in the reflux line. Carbon dioxide gas was passed in at a rate of 10 cc. per minute and the vessel contents heated to reflux and maintained thereat for 4 hours.

Xylene was removed under vacuum to give 45.3 parts of a pale yellow liquid having a fluorine content of 20%.

Lacquer preparation

A lacquer of the following composition was prepared:—

	Parts
Nitrocellulose as used in Example 1 but of viscosity such that 20 g. (dry) dissolved in 100 cc. of a mixture of 95 volumes acetone and 5 volumes water was between 25 and 45 poises at 20°C	10 (as dry)
Blown linseed oil 90 poise viscosity at 20°C	8
Blown castor oil 90 poise viscosity at 20°C	4.5
Fluorine-containing castor oil ester (as prepared above)	2.5
Solvent	70

The solvent composition was:—

	Parts
Butyl acetate	15
n-butanol	10
Ethyl acetate	20
Isopropanol	9
Methyl cyclohexanone	10
Toluene	36

When sprayed on leather the film formed showed improved soil, water and grease resistance as compared with a film from the same composition but omitting the fluorine-containing ester.

EXAMPLE 15

A lacquer of the following composition was prepared:—

	Parts
Nitrocellulose (as used in Example 14)	30 (as dry)
Titanium dioxide	21
Solvent (as used in Example 14)	217.5

The above composition was ball milled for 24 hours and there were then added:—

	Parts
Blown linseed oil 90 poises	16.8
Blown castor oil 90 poises	9.5

The resultant lacquer was divided and to one half were added 2 parts of the fluorinated castor oil ester prepared in Example 14 and to the other half were added 2 parts of ordinary castor oil.

The formulations were sprayed on to leather to form films. The film containing the fluorinated castor oil ester was superior in soil, water and grease resistance to that containing ordinary castor oil.

EXAMPLE 16

A lacquer of the following composition was prepared:—

	Parts
Nitrocellulose (as used in Example 14)	28.6
Dibutyl phthalate	4
Dicyclohexyl phthalate	5.5
Castor oil	0.7
Fluorine-containing castor oil ester (as prepared in Example 14)	3.3
74 O.P. Industrial Methylated Spirits	26.1
Ethyl acetate	21.4
Butyl acetate	5.2
n-butanol	5.2

The lacquer, applied to paper by brushing, gave a film which was superior in soil, water and grease resistance to a film made from a lacquer of the same composition from which the fluorine-containing ester was omitted.

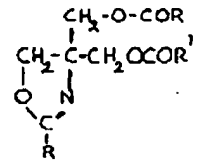
EXAMPLE 17

Preparation of fluorine-containing ester

30 parts trimethylol amino methane ('tris amino'), 50 parts lauric acid and 20 parts xylene were mixed in a 3-necked stirred reaction flask fitted with a gas inlet and a Dean and Stark apparatus. Carbon dioxide gas was passed in at a rate of 10 cc. per minute and the mixture in the flask heated at 200°C for 1 hour. After cooling to 120°C, a further 50 parts lauric acid were added and again the contents of the flask were heated at 200°C for 1½ hours. The xylene was removed by vacuum distillation to give a pale yellow liquid, a lauric 'diester'.

4.7 parts of this 'diester', 4.0 parts pentadecafluorooctanoic acid and 15 parts xylene were mixed in a 3-necked stirred reaction flask fitted with a gas inlet and condenser. Carbon dioxide was passed in at a rate of 10 cc. per minute and the mixture was heated under reflux for 4 hours. The xylene was removed by vacuum distillation to give fluorinated oxazoline as a cream coloured, waxy solid having an acid value of 15 mg. KOH/g. and a fluorine content of 30.6%.

The product had the formula:—



where R=lauryl group
and R'=pentadecafluorooctanyl group

Lacquer preparation

The product prepared above was incorporated in a lacquer of the following composition:—

	Parts
Nitrocellulose (as used in Example 1)	40
Resin A (as used in Example 1)	40
Di-isooctyl phthalate	10
Fluorinated oxazoline as described above	10
Solvent (as used in Example 6)	150

The lacquer was sprayed on to wood. The resultant film was superior in soil, water and grease resistance to a film prepared from the same lacquer composition from which the fluorinated oxazoline was omitted.

EXAMPLE 18

A lacquer of the following composition was prepared:—

	Parts
Titanium dioxide	6.2
Carbon black	0.1
40% solution in a mixture of 30 volumes acetone and 70 volumes toluene of polymethyl methacrylate of inherent viscosity 0.34	4
Ethylene glycol monoethyl ether acetate	2.5

The above ingredients were ball milled for 24 hours and there were then added the following:—

	Parts
40% solution of polymethyl methacrylate as used above	17.9
Butyl benzyl phthalate	3.0
Fluoroalkyl phthalate containing 60% fluorine (as prepared in Example 2)	0.80
Ethylene glycol monoethyl ether acetate	17.9
methyl ethyl ketone	23.8
Toluene	23.8

The lacquer was sprayed on to metal and gave a film with improved soil, water and grease resistance as compared with a film prepared from the same lacquer composition from which the fluorinated ester was omitted.

EXAMPLE 19

A lacquer was prepared in the same way as for example 18 but in place of the fluoroalkyl phthalate containing 60% fluorine, 0.80 parts of pentaerythritol triacetate monopentadecafluorooctanoate (43% fluorine) as used in Example 1 were used. The resulting lacquer was sprayed on to wood and gave a film with improved soil, water and grease resistance as compared with a film prepared from the same lacquer composition but omitting the fluorinated pentaerythritol ester.

EXAMPLE 20

The rosin used in this Example was a commercial rosin consisting essentially of about 90% of rosin acids. These are isomeric C_{20} acids (such as, for example, abietic acid) containing the phenanthrene nucleus.

The rosin E used in this Example was a rosin/maleic anhydride condensate esterified with glycerol having an acid value less than 32 mg. KOH/g.

Preparation of fluorine-containing ester

40 parts of fluorinated alcohol of formula $H(CF_2)_6CH_2OH$, 30 parts of commercial rosin and 0.05 parts of sulphuric acid were mixed in a stirred reaction vessel fitted with a stirrer, gas inlet and a reflux condenser. Carbon dioxide was passed in at a rate of 10 cc. per minute and the vessel contents were heated and allowed to reflux at 170°C until the acid value fell below 40 mg. KOH/g. (approximately 13 hours).

The excess alcohol was then distilled off. The vessel contents were cooled, extracted with water and finally dried under vacuum to give 62 g. of a fluorinated rosin ester as a hard, transparent, yellow, brittle solid.

Lacquer preparation

A lacquer of the following composition was prepared:—

	Parts
Nitrocellulose (as used in Example 1)	12.3
Fluorinated rosin ester (prepared as above)	13.3
Resin E	8.6
Dibutyl phthalate	1.8
Butyl acetate	25.0
Toluene	40.0
Methyl ethyl ketone	21.0
Methyl isobutyl ketone	14.0

The lacquer was sprayed on to wood. The resulting film had a better water and oil repellency and better soil and stain resistance than a film prepared from the same lacquer composition from which the fluorine-containing rosin ester was omitted.

EXAMPLE 21

Preparation of fluorine-containing ester

22.5 parts of rosin, 45.0 parts of fluorine-containing alcohol of formula $H(CF_2)_{10}CH_2OH$ and 0.05 parts of sulphuric acid were mixed in a reaction vessel fitted with a stirrer, gas inlet and a reflux condenser. Carbon dioxide was passed in at a rate of 10 cc. per minute and the vessel contents were heated and allowed to reflux at 235°C until the acid value fell below 20 mg. KOH/g.

The excess alcohol was then distilled off. The vessel contents were cooled, extracted with water and finally dried under vacuum to give 62 g. of a fluorinated rosin ester as a hard, yellow solid.

Lacquer preparation

A lacquer of the following composition was prepared:—

	Parts
Nitrocellulose (as used in Example 1)	12.3
Fluorinated rosin ester (prepared as above)	13.3
Resin E (as used in Example 20)	8.6
Dibutyl phthalate	1.8
Butyl acetate	25.0
Toluene	40.0
Methyl ethyl ketone	21.0
Methyl isobutyl ketone	14.0

The lacquer was sprayed on to wood. The resulting film had a higher water and oil repellency and better soil and stain resistance than a film made from the same lacquer composition from which the fluorinated rosin ester was omitted.

EXAMPLE 22

Preparation of fluorine-containing ester

42.5 parts rosin as used in Example 20 and 2.5 parts of maleic anhydride were mixed in a stirred reaction vessel fitted with a gas inlet and reflux condenser. Carbon dioxide was passed in at a rate of 10 cc. per minute and the temperature raised to 180°C and maintained thereat for 1 hour.

The vessel contents were cooled to below 100°C and 76 parts of a fluorine-containing alcohol of formula $H(CF_2)_mCH_2OH$ were added. Heating was resumed and the temperature maintained at reflux until the acid value fell below 40 mg KOH/g.

98 parts of fluorinated maleinised rosin ester were obtained as a hard, yellow, brittle solid.

Lacquer preparation

A lacquer of the following composition was prepared:—

	Parts
Nitrocellulose (as used in Example 1)	12.3
Fluorinated maleinised rosin ester (prepared as above)	8.6
Ester gum (glycerol ester of rosin)	13.3
Dibutyl phthalate	1.8
Butyl acetate	25.0
Toluene	40.0
Methyl ethyl ketone	21.0
Methyl isobutyl ketone	14.0

The lacquer was sprayed on to metal. The resultant film was superior in soil, water and grease resistance to a film prepared from the same lacquer composition but omitting the fluorinated ester.

EXAMPLE 23

The nitrocellulose used in the Example had a nitrogen content between 11.2 and 11.8% and was 'damped' with isopropanol in the ratio of 70 parts nitrocellulose to 30 parts isopropanol. 40 g. of this nitrocellulose dried and dissolved in 100 cc. aqueous acetone, prepared by mixing 95 volumes acetone and 5 volumes water, had a viscosity of 30 to 50 poises at 20°C.

Preparation of fluorine-contain ester

β-perfluorotrialkyl propionic acid having the formula $(C_2F_5)_2(CF_3)C.CH_2COOH$ was made by adding tetrafluoroethylene pentamer $(C_2F_4)_5$ to a stirred aqueous solution of potassium hydroxide or sodium hydroxide containing 30% to 60% by weight of the hydroxide at such a rate as to maintain the system in steady reflux without the application of external heat. The weights of pentamer and hydroxide were approximately equal, and after all the pentamer had been added, the reaction mixture was refluxed for 1 to 2 hours. On cooling the potassium or sodium salt of the acid crystallised and after separation was dissolved in water and the cold solution acidified with sulphuric acid. The acid separated as a lower layer which solidifies and can be recrystallised from acetone to give a white solid melting at about 57°C.

5 parts of the acid were mixed with 10 parts of purified thionyl chloride and heated under reflux for 2 hours a 45°C and a further 4 hours at 75°C. Excess thionyl chloride was distilled off, leaving a residue of β-perfluorotrialkyl propionyl chloride.

0.5 parts of sodium metal were reacted with 5 parts of the monoethyl ether of diethylene glycol in 35 parts of toluene and the solution was added to the β-perfluorotrialkyl propionyl chloride prepared above. The resulting mixture was heated to 115°C for 6 hours and the toluene was distilled off at atmospheric pressure. The residue was distilled under reduced pressure and a fraction of the distillate collected in the boiling range 55—85°C at a pressure of 2 mm. This fraction was redistilled and gave the ester of diethylene glycol monoethyl ether and β-trifluoromethyl bis(β-pentafluoroethyl)propionic acid boiling at 75—80°C at 1 mm. and containing 39% fluorine.

Lacquer preparation

A lacquer of the following composition was prepared:—

	Parts
Nitrocellulose	10 (as dry)
Fluorinated ester (as prepared above)	1
Ethyl acetate	25
n-butyl acetate	25
n-butyl alcohol	10
Toluene	40

This lacquer was applied to cardboard and gave a film with improved soil, water and grease resistance as compared with a film from the same composition from which the fluorinated ester was omitted.

EXAMPLE 24

	Parts
Ethyl cellulose (as used in Example 11)	20
Fluorinated ester (as prepared in Example 23)	
74 O.P. Industrial methylated Spirits	20
Toluene	80

This lacquer was applied to cardboard and gave a film with improved soil, water and grease resistance as compared with a film from the same composition from which the fluorinated ester was omitted.

EXAMPLE 25

	Parts
Cellulose acetate (as used in Example 9)	15
Fluorinated ester (as prepared in Example 23)	0.4
Acetone	50
Ethyl acetate	15
74 O.P. Industrial Methylated Spirits	15
Ethyl lactate	5

This lacquer was applied to cardboard and gave a film with improved soil, water and grease resistance as compared with a film from the same composition from which the fluorinated ester was omitted.

It is to be noted that the fluorine-containing esters which may be included in the film-forming compositions of the present invention are not formed by condensation polymerisation and therefore are not to be confused with the polymeric fluorine-containing condensation esters used in the compositions described and claimed in our co-pending Application No. 11955/67 (Serial No. 1157319).

WHAT WE CLAIM IS:—

1. A film-forming composition comprising a film-forming polymeric material and a fluorine-containing ester containing a chain of at least 3 carbon atoms in which at least half of the carbon valencies other than carbon to carbon are satisfied by a fluorine atom, the quantity of ester being such that the fluorine content of the composition is in the range of 0.1 to 30%.

2. A composition as claimed in Claim 1 wherein the fluorine-containing ester is derived from a fluorine-containing carboxylic acid of the formula R^F—COOH wherein R^F denotes a fluorinated alkyl group.

3. A composition as claimed in Claim 2 wherein the R^F group is a straight or branched chain alkyl group of 4 to 18 carbon atoms in which at least half of the hydrogen atoms are replaced by fluorine atoms.

4. A composition as claimed in Claim 2 or Claim 3 wherein the R^F group is a perfluorobutyl or a perfluoroheptyl or a bis(2-pentafluoroethyl)2 - trifluoromethyl ethyl group.

5. A composition as claimed in any one of Claims 1 to 4 wherein the fluorine-containing ester is an ester of castor oil, ethylene glycol, polyethylene glycol, glycerol, trimethylolpropane, trimethylolethane, mono- and dipentaerythritol, trimethylol amino methane or diethylene glycol monoether.

6. A composition as claimed in Claim 1 wherein the fluorine-containing ester is derived from an alcohol containing fluorine atoms.

7. A composition as claimed in Claim 6 wherein the fluorine-containing ester is derived from an alcohol of the formula $R^F(CH_2)_nOH$ wherein R^F denotes a fluorinated alkyl group and n is an integer from 1 to 3.

8. A composition as claimed in Claim 7 wherein the R^F group of the alcohol is a straight or branched chain alkyl group of 3 to 18 carbon atoms wherein at least half of the hydrogen atoms are replaced by fluorine atoms.

9. A composition as claimed in Claim 8 wherein the R^F group is a perfluoropropyl, perfluorobutyl, perfluorohexyl, perfluorooctyl or a perfluorodecyl group.

10. A composition as claimed in any one of Claims 7 to 9 wherein the fluorine-containing ester is an ester of phosphoric, phthalic, adipic, sebacic, tartaric, citric, stearic or abetic acid, or the adduct of abietic acid and maleic anhydride or the carboxylic acid of the formula R^F—COOH wherein R^F denotes a fluorinated alkyl group.

11. A composition as claimed in any one of Claims 1 to 10 wherein the film-forming polymeric material comprises nitrocellulose, cellulose acetate, cellulose acetate butyrate, ethyl cellulose, polymethyl methacrylate, polyvinyl chloride, polyvinyl acetate or copolymers thereof.

12. A film-forming composition substantially as herein described with reference to any of the Examples.

13. A lacquer solution compriaing a film-forming composition as claimed in any one of Claims 1 to 12.

THOMAS J. REID,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25, Southampton Buildings, London, W.C.2. from which copies may be obtained.